

METHOD OF PRODUCING OPTICAL FIBER PREFORM, AND  
OPTICAL FIBER PREFORM AND OPTICAL FIBER PRODUCED WITH THE  
METHOD

5      BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of producing an optical fiber preform with the collapsing process and to an optical fiber preform and an optical fiber produced with the method.

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Description of the Background Art

The collapsing process is a process to produce an optical fiber preform by collapsing a glass pipe to form a solid body. The collapsing operation may be performed with a glass rod inserted into a glass pipe. In this case, the glass

15     pipe and the glass rod are unified. Figure 17 is a schematic diagram showing the collapsing process. A glass rod 2 is inserted in a glass pipe 1. The glass pipe 1 is held by holding portions 4 of a glass-processing lathe 13. While the glass pipe 1 is rotated together with the glass rod 2, one end of the glass pipe is sealed by heating it with a heat source 3. Then, the heat source 3 is moved to  
20     collapse the glass pipe by heating it. The following techniques are also known:

(a) Before the collapsing operation, the surface of the glass is chemically purified by heating the glass pipe 1 while a chlorine gas is blown into it. (b) The collapsing operation is performed while the inside of the glass pipe 1 is evacu-

ated with a vacuum pump. (See the published Japanese patent application *Tokukaihei 8-225335*.)

Phenomena of occlusion of water into silica glass and its release are explained in a reference book entitled "Application handbook for amorphous silica materials" (compiled by *Katsuro Fukamizu*, published by Realize Co., 1999, pp. 56-57). Phenomena of diffusion of water into silica glass are explained in a report by *Hajimu Wakabayashi* and *Minoru Tomozawa*, "Diffusion of water into silica glass at low temperature" (*J. Am. Ceram. Soc.*, Vol. 72, No. 10, pp. 1850-55, 1989).

10      Figure 18 is a graph showing an increment in transmission loss at a  $1.4\text{-}\mu\text{m}$  wavelength band due to OH groups. OH groups in silica glass have a high absorption peak (OH absorption) in the vicinity of  $1.4\text{ }\mu\text{m}$  in wavelength. The OH absorption increases the transmission loss at a  $1.4\text{-}\mu\text{m}$  band (OH-originated loss) and makes it difficult to transmit signals in the  $1.4\text{-}\mu\text{m}$  band  
15     and excitation light for Raman amplification. Therefore, it is desirable to minimize the OH absorption. However, when an optical fiber preform is produced with the collapsing process, it has been difficult to reduce the OH absorption.  
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## 20      SUMMARY OF THE INVENTION

An object of the present invention is to offer a method of producing with the collapsing process an optical fiber preform capable of forming an optical fiber in which an increment in transmission loss due to the OH absorption is reduced

and to offer an optical fiber preform and an optical fiber produced with the method.

According to the present invention, the foregoing object is attained by offering the following method of producing an optical fiber preform. The method comprises:

- (a) a drying step to reduce the amount of hydrogen atom-containing substances in a glass pipe;
- (b) a sealing step to seal one end of the glass pipe; and
- (c) a collapsing step to collapse the glass pipe to obtain a solid body.

According to one aspect of the present invention, the present invention offers the following method of producing an optical fiber preform. The method comprises:

- (a) a drying step to heat a glass pipe at a temperature of 550 °C or below;
- (b) a sealing step to seal one end of the glass pipe; and
- (c) a collapsing step to collapse the glass pipe to obtain a solid body.

According to another aspect of the present invention, the present invention offers an optical fiber preform produced through the following steps:

- (a) heating a glass pipe at a temperature of 550 °C or below;
- (b) sealing one end of the glass pipe; and
- (c) collapsing the glass pipe to obtain a solid body.

The optical fiber preform's portion formed by the interface portion at the time of the collapsing contains OH groups at a concentration of 100 wt. ppb or below.

According to yet another aspect of the present invention, the present inven-

tion offers an optical fiber produced by drawing an optical fiber preform produced through the following steps:

- (a) heating a glass pipe at a temperature of 550 °C or below;
- (b) sealing one end of the glass pipe; and
- 5 (c) collapsing the glass pipe to obtain a solid body.

The optical fiber has an OH-originated loss of less than 0.5 dB/km at a wavelength of 1.38 μm.

In this specification, the optical fiber preform may be a glass body from which an optical fiber can be formed by directly drawing the glass body. The optical  
10 fiber preform may also be a glass body (an intermediate of an optical fiber preform) to be further processed for the subsequent drawing.

Advantages of the present invention will become apparent from the following detailed description, which illustrates the best mode contemplated to carry out  
15 the invention. The invention can also be carried out by different embodiments, and their details can be modified in various respects, all without departing from the invention. Accordingly, the accompanying drawing and the following description are illustrative in nature, not restrictive.

## 20 BRIEF DESCRIPTION OF THE DRAWING

The present invention is illustrated to show examples, not to show limitations, in the figures of the accompanying drawing. In the drawing, the same reference numerals refer to similar elements.

In the drawing:

Figures 1A and 1B are schematic diagrams showing the "blowing-away purging," one of the embodiments of the drying step of the present invention, in which Fig. 1A shows the diagram when only a glass pipe is treated and Fig. 1B shows the diagram when a glass rod is inserted in the glass pipe.

Figures 2A to 2D are schematic diagrams showing the "cyclic purging," one of the embodiments of the drying step of the present invention, in which Figs. 2A to 2C show the diagrams when the glass pipe has a through hollow and Fig. 2D shows the diagram when the glass pipe is sealed at some midpoint.

Figure 3 is a schematic diagram showing a glass pipe having connected holding pipes.

Figures 4A to 4C are schematic diagrams showing an embodiment of the connecting step of the present invention.

Figure 5 is a schematic diagram showing an embodiment of the etching step of the present invention.

Figure 6 is a flow chart for Example 1.

Figure 7 is a flow chart for Example 2.

Figure 8 is a schematic diagram showing an embodiment of the chemically purifying step of the present invention.

Figures 9A and 9B are schematic diagrams showing an embodiment of the sealing step of the present invention.

Figures 10A and 10B are schematic diagrams showing an embodiment of the collapsing step of the present invention.

Figure 11 is a graph showing the amount of the water desorbing from a heated silica-glass body.

Figure 12 is a schematic diagram showing an embodiment of the holding pipe of the present invention.

5      Figure 13 is a diagram showing the refractive-index profile of the optical fiber produced in Example 1.

Figure 14 is a graph showing the transmission loss-wavelength properties of the optical fibers produced in Example 1 and Comparative example 1.

10     Figure 15 is a diagram showing the refractive-index profile of the optical fiber produced in Example 2.

Figure 16 is a graph showing the transmission loss-wavelength property of the optical fiber produced in Example 2.

Figure 17 is a schematic diagram showing the collapsing process.

15     Figure 18 is a graph showing an increment in transmission loss at a  $1.4\text{-}\mu\text{m}$  wavelength band due to OH groups.

## DETAILED DESCRIPTION OF THE INVENTION

Here is a silica-glass body having on its surface adsorbed hydrogen atom-containing substances, such as hydrogen atom (H), hydrogen molecules ( $\text{H}_2$ ),  
20    water ( $\text{H}_2\text{O}$ ), methanol ( $\text{CH}_3\text{OH}$ ), methane ( $\text{CH}_4$ ), and ketone ( $\text{CH}_3\text{COCH}_3$ ). When the silica-glass body is heated, the hydrogen atom contained in the hydrogen atom-containing substances reacts with the glass body at its surface as shown by chemical formulae (1) and (2).



The hydroxyl group (OH group) thus produced is difficult to remove.

For example, when the hydrogen atom-containing substance is H<sub>2</sub>O, a heating treatment causes the H<sub>2</sub>O to be chemically adsorbed onto the surface of the glass. When the heating treatment is performed at a temperature over 550 °C, the activation energy of the adsorption becomes twice as high as that produced at low temperatures, making it difficult to remove the H<sub>2</sub>O from the surface of the glass. When heated at a temperature of 600 °C or above, the H<sub>2</sub>O reacts with the glass at its surface to form an OH group. Even when the heating is performed at a temperature as low as 200 °C or above, the H<sub>2</sub>O may react with the glass.

According to the present invention, the method of producing an optical fiber preform performs the following treatment before a glass pipe is transformed into a solid body by the collapsing process. The treatment is performed to reduce the hydrogen atom-containing substances adsorbed on the inner surface of the glass pipe or the hydrogen atom-containing substances contained in the atmosphere in the glass pipe or both. In this specification, the treatment that reduces not only H<sub>2</sub>O but also other hydrogen atom-containing substances is referred to as "drying" and the step that performs the drying is referred to as a "drying step." The drying treatment eliminates the formation of OH groups even when the glass pipe is heated at high temperatures in the collapsing step. As a result, the drying treatment enables the production of an optical fiber pre-

form that can reduce the increment in the transmission loss due to the OH absorption in the optical fiber. When the drying step of the present invention is performed, the concentration of the OH groups remaining at the optical fiber preform's portion formed by the interface portion at the time of the collapsing 5 can be reduced to 100 wt. ppb or below. Furthermore, the OH-originated loss of the optical fiber can be reduced to less than 0.5 dB/km at a wavelength of 1.38  $\mu\text{m}$ .

The drying step is performed at a temperature of 550  $^{\circ}\text{C}$  or below. If the heating temperature exceeds 550  $^{\circ}\text{C}$ , it becomes difficult to remove  $\text{H}_2\text{O}$  and 10 other substances adsorbed on the silica glass. If the temperature exceeds 600  $^{\circ}\text{C}$ , the  $\text{H}_2\text{O}$  and other substances react with the glass at its surface to form OH groups.

The types of embodiments for the drying step include the following embodiments:

- 15 (A) Hydrogen atom-containing substances in the glass pipe are purged by blowing a gas having a low concentration of hydrogen atom-containing substances (a dried gas) from one end of the glass pipe to the other (hereinafter referred to as "blowing-away purging").
- (B) The inside of the glass pipe is evacuated with a vacuum pump (hereinafter 20 referred to as "evacuation").
- (C) The inside of the glass pipe is evacuated with a vacuum pump while the blowing-away purging is performed.
- (D) First, the gas in the glass pipe is discharged to reduce the pressure inside

the pipe. Second, a dried gas is introduced into the pipe to raise the pressure inside the pipe. This cycle is performed at least once (hereinafter referred to as "cyclic purging").

(E) A combination of embodiments (A) to (D), such as (B) + (A), (C) + (A), (B) +

5 (C) + (D), (B) + (D), or (C) + (D).

The drying step can nearly completely remove not only hydrogen atom-containing substances adsorbed both on the inner surface of the glass pipe and on the glass rod inserted in the glass pipe but also hydrogen atom-containing substances contained in the atmosphere in the glass pipe. For example, adsorbed water can be reduced to about  $10^2$  wt. ppm or below.

10 Embodiment (A), expressed as the "blowing-away purging," is explained below. Figures 1A and 1B are schematic diagrams showing the "blowing-away purging," one of the embodiments of the drying step of the present invention.

Figure 1A shows the diagram when only a glass pipe is treated. Figure 1B

15 shows the diagram when a glass rod is inserted in the glass pipe.

As shown in Fig. 1A, a glass pipe 1 whose both ends are open is held by holding portions 4. A dried gas is introduced into the glass pipe 1 from a gas line 5 attached to one end of the glass pipe 1 to perform the blowing-away purging through a gas line 6 attached to the other end of the pipe. In the case

20 of Fig. 1B, under the condition that a glass rod 2 is inserted in a glass pipe 1, a dried gas is introduced into the glass pipe 1 from a gas line 5 attached to one end of the pipe 1 to perform the blowing-away purging through a gas line 6 attached to the other end of the pipe.

When the blowing-away purging is performed, the glass pipe may be heated. It is desirable that the heating be performed with a cylindrical mantle heater 7, a tape heater 7' wound on the outer surface of the glass pipe 1, or an electric furnace to facilitate the temperature control. The heating may be performed 5 with another means such as an oxyhydrogen burner or a plasma burner. It is possible to perform the blowing-away purging for a prolonged period without heating.

As explained above, the blowing of a dried gas from one end to the other can not only desorb hydrogen atom-containing substances adsorbed on the inner 10 surface of the glass pipe 1 and on the surface of the glass rod 2 but also reduce the amount of the hydrogen atom-containing substances in the atmosphere in the glass pipe 1. In addition, this process reduces the amount of the re-adsorption of the desorbed hydrogen atom-containing substances onto the surface of the glass.

15 The types of dried gas for the purging in the drying step include an inert gas, such as nitrogen ( $N_2$ ), helium (He), or argon (Ar), a reactive gas, such as chlorine ( $Cl_2$ ) or thionyl chloride ( $SOCl_2$ ), and an oxygen gas ( $O_2$ ). It is desirable that the dried gas contains hydrogen atom-containing substances at a concentration of 10 vol. ppm or less in total, more desirably 1 vol. ppm or less.

20 It is desirable that in the drying step, the volume of the gas blown per minute is at least 10 times the inner volume of the glass pipe in the longitudinal range heated in the drawing step. The sufficient volume of the gas reduces a back diffusion of the hydrogen atom-containing substances from the downstream.

It is desirable that the blowing-away purging be carried out for at least one hour in the drying step. The long-time purging can sufficiently reduce the amount of the adsorbed hydrogen atom-containing substances.

When the glass pipe 1 is heated during the blowing-away purging, the adsorbed molecule can obtain energy to desorb from the surface of the glass, so that the time for the purging can be shortened. Figure 11 is a graph showing the amount of the water desorbing from a heated silica-glass body. As can be seen from Fig. 11, there exist two types of adsorbed H<sub>2</sub>O: one is the H<sub>2</sub>O whose desorption can be promoted at 60 °C or higher (peak I) because it is weakly bonded to the surface of the glass and the other is the H<sub>2</sub>O whose desorption can be promoted at 400 °C or higher (peak II) because it is strongly bonded to the surface of the glass. It is desirable to heat the glass pipe at a temperature of 60 °C or higher. It is also desirable to heat the glass pipe at 100 °C or higher because H<sub>2</sub>O has a boiling point of 100 °C at atmospheric pressure.

15 It is desirable to heat the glass pipe at a temperature lower than 200 °C.

When the blowing-away purging is performed at a temperature lower than 200 °C, the formation of OH groups can be suppressed. If the temperature is 200 °C or higher, H<sub>2</sub>O may react with the glass at its surface.

It is also desirable to heat the glass pipe at a temperature of 60 °C or higher and lower than 200 °C to desorb the weakly bonded H<sub>2</sub>O from the surface of the glass (the amount of this H<sub>2</sub>O is large) and then raise the temperature to 300 °C or higher. Undoubtedly, the blowing-away purging at room temperature

can also reduce the amount of the hydrogen atom-containing substances.

In the drying step, it is desirable to heat the glass pipe at a wider longitudinal range than that heated at 550 °C or higher in the sealing step or the collapsing step. In Fig. 1B, range A shows the range corresponding to the effective

5 portion of the optical fiber preform to be formed by the collapsing operation (the effective portion is the portion of the optical fiber preform to be used as the final product). Range A is heated at 550 °C or higher in the collapsing step.

Range B shows the range to be heated in the drying step. As shown in Fig. 1B,

range B is wider than range A. This arrangement can prevent OH groups con-

10 tained in the glass pipe in range B from leaving the glass pipe to form H<sub>2</sub>O and then being re-adsorbed onto the inner surface of the glass pipe in range A.

Embodiment (B), expressed as the "evacuation," is explained below. In this embodiment, it is desirable to evacuate with a vacuum pump the inside of the glass pipe to an absolute pressure of 4 kPa or below, more desirably 0.4 kPa or

15 below, preferably 0.04 kPa or below. H<sub>2</sub>O has a saturated vapor pressure of 4 kPa at a temperature of 25 °C. Therefore, when the internal pressure of the

glass pipe is reduced to a value lower than this value, the desorption of the H<sub>2</sub>O can be promoted. Furthermore, the reduction in the internal pressure can increase the mean free path for the H<sub>2</sub>O and therefore reduce the possibility of

20 its collision onto the wall of the glass. As a result, the re-adsorption of the H<sub>2</sub>O onto the surface of the glass can be significantly suppressed.

Embodiment (D), expressed as the "cyclic purging," is explained below. Figures 2A to 2D are schematic diagrams showing the "cyclic purging," one of the

embodiments of the drying step of the present invention. Figures 2A to 2C show the diagrams when the glass pipe has a through hollow. Figure 2D shows the diagram when the glass pipe is sealed at some midpoint. In this embodiment, it is desirable to reduce the pressure to 4 kPa or below in the 5 pressure-reducing step. It is desirable to raise the pressure to 50 kPa or above in the pressure-raising step, more desirably 100 kPa or above.

When the glass pipe has a through hollow, the cyclic purging is carried out by performing at least once the following procedure from (a) to (c), for example:

(a) A valve 9 is closed and a valve 10 is opened to evacuate the glass pipe.

10       $\longleftrightarrow$  The valve 9 is opened and the valve 10 is closed to introduce a dried gas into the glass pipe. (See Fig. 2A.)

(b) The valve 9 is kept open and the valve 10 is opened to evacuate the glass pipe while introducing a dried gas.

$\longleftrightarrow$  The valve 9 is kept open and the valve 10 is closed. (See Fig. 2B.)

15      (c) The valve 9 is closed and the valve 10 is opened to evacuate the glass pipe.

$\longleftrightarrow$  The valve 9 is opened and the valve 10 is kept open to evacuate the glass pipe while introducing a dried gas. (See Fig. 2C.)

In step (c), when the flow rate of the dried gas is increased and the rate of the 20 evacuation is decreased, the inside of the glass pipe can also be pressurized even while the evacuation is continued.

When the glass pipe is sealed at some midpoint, the cyclic purging is carried out through the following procedure. (See Fig. 2D.) In this case, a gas line 8,

which is connected to a vacuum pump, is connected to a gas line 5 attached to the end of the glass pipe for introducing a gas. First, a valve 9 is closed and a valve 13 is opened to evacuate the glass pipe 11 through the gas lines 5 and 8. This evacuation reduces the internal pressure of the glass pipe 11 to an absolute pressure of 4 kPa or below, for example, to evaporate adsorbed water and other substances. Next, the valve 9 is opened to introduce a dried gas into the glass pipe, and at the same time the valve 13 is closed to raise the internal pressure of the glass pipe to an absolute pressure of 50 kPa or above, for example. When the evacuation and the gas introduction are conducted alternately at least once, the amount of the hydrogen atom-containing substances adsorbed on the surfaces of the glass pipe and the glass rod can be significantly reduced.

A holding pipe may be connected to one end or both ends of the glass pipe to perform the collapsing operation of the present invention. In other words, before the drying step, another step may be introduced to connect a holding pipe to at least one end of the glass pipe. Figure 3 is a schematic diagram showing the glass pipe having the connected holding pipes. A holding pipe 12 is connected to both ends of a glass pipe 11, which is to be used as the effective portion in the optical fiber preform. This method has an advantage in that the use of the costly glass pipe can be reduced to a required minimum.

When a holding pipe is connected to the glass pipe to perform the collapsing operation of the present invention, it is desirable that the holding pipe have few hydrogen atom-containing substances adsorbed on its inner surface and contain a low concentration of OH groups in its body. More specifically, it is de-

sirable that the holding pipe contain OH groups at a concentration of 10 wt. ppm or less. The reason is that when the holding pipe is heated during the glass-pipe sealing step and the collapsing step, OH groups contained in the holding pipe may leave the holding pipe to form H<sub>2</sub>O and then be re-adsorbed 5 onto the inner surface of the glass pipe in the effective portion.

It is desirable that the holding pipe be provided with a portion that radiates to the outside of the pipe the infrared rays travelling through the solid portion forming the wall of the pipe. Figure 12 is a schematic diagram showing an embodiment of the holding pipe of the present invention, in which the holding 10 pipe is connected to the glass pipe 11. A holding pipe 16 is provided with a radiating portion 15 that has the shape of a knot formed by using the pipe. When the holding pipe 16 is heated with a heat source 3, the temperature of the portion of the holding pipe 16 opposite to the heat source 3 with respect to the radiating portion 15 is lower than the temperature when no radiating portion is 15 provided. For example, when one end of a holding pipe was heated at 1,400 °C for 10 minutes, the temperature of the portion of the holding pipe 1,000 mm apart from the heat source 3 was 50 °C when the radiating portion 15 was provided between the portion and the heat source 3 and 100 °C when no radiating portion was provided.

20 When the holding pipe 16 is used, the portion between the radiating portion 15 and the glass pipe 11 is subjected to the drying step of the present invention to remove hydrogen atom-containing substances. The portion of the holding pipe 16 opposite to the glass pipe 11 with respect to the radiating portion 15 is

not heated to high temperatures. Consequently, hydrogen atom-containing substances adsorbed in this portion do not diffuse toward the effective portion of the glass pipe 11 during the production process.

The radiating portion 15 may have a shape other than the shape of a knot formed by using the pipe. For example, an opaque silica-glass pipe capable of scattering infrared rays may be inserted into the holding pipe 16 to form the radiating portion 15. Alternatively, when two pipes are connected to form the holding pipe 16, the fusion-connected portion may be used as the radiating portion 15.

Figures 4A to 4C are schematic diagrams showing an embodiment of the connecting step of the present invention. The connection between the glass pipe 11 and the holding pipe 12 is performed by heating the two members with a heat source 3 so that they can be fusion-connected. When a plasma burner, an induction furnace, a resistance furnace, or another heat source that does not produce H<sub>2</sub>O is used, the intrusion of H<sub>2</sub>O can be reduced significantly at the time of the connection between the glass pipe and the holding pipe. On the other hand, when an oxyhydrogen burner or another heat source that produces H<sub>2</sub>O is used, hydrogen atom-containing substances may intrude into the glass pipe and the holding pipe at the time of the connection between the two members.

To prevent the above-described intrusion, as shown in Fig. 4A, for example, a dried gas is introduced into both pipes from the end opposite to the end to be connected. Alternatively, as shown in Fig. 4B, one of the two pipes is provided

with a sealing material 14 attached to its end opposite to the end to be connected. Under this condition, a dried gas is introduced into the other pipe from its end opposite to the end to be connected. Yet another alternative is shown in Fig. 4C. In this case, each pipe is provided with a sealing material 5 14 attached to its end opposite to the end to be connected. When the connection work is conducted under this condition, the amount of the outside air entering the glass pipe can be reduced. As a result, contamination of the inner surfaces of the two pipes can be reduced. The dried gas can be the same type of the dried gas as used in the drying step. It is desirable that the dried gas 10 contains hydrogen atom-containing substances at a concentration of 10 vol. ppm or less in total, more desirably 1 vol. ppm or less. It is also desirable to perform the drying step after the connecting step. This is another desirable embodiment.

It is desirable that the collapsing operation of the present invention include a 15 step in which the inner surface of the glass pipe is gas phase-etched before or after the drying step (this step is called an "etching step") (the term "glass pipe" is used as a generic term that includes a glass pipe having a holding pipe connected to at least one end of it). The gas-phase etching has the following effects:

- 20 (a) It can smooth the inner surface of the glass pipe.  
(b) It can shave off chemically adsorbed hydrogen atom-containing substances that still remain after the drying step.  
(c) It can remove impurities having intruded into the pipe to a certain extent

(from several microns to several millimeters from the inner surface).

Figure 5 is a schematic diagram showing an embodiment of the etching step of the present invention. The glass pipe 1 is heated with a heat source 3 while an etching gas is introduced into the pipe from one end of it. Range A shows 5 the range corresponding to the effective portion of the optical fiber preform. Range A is heated at 550 °C or higher in the following step, for example, the collapsing step. Range C shows the range to be gas phase-etched. It is desirable that range C include range A. The reason is that if the chemically adsorbed H<sub>2</sub>O still remains on the inner surface of the glass pipe in range A, this 10 arrangement can prevent the H<sub>2</sub>O from evaporating to contaminate the inside of the glass pipe when the glass pipe is heated at 550 °C or higher at the collapsing step.

The types of gas for the gas-phase etching include sulfur hexafluoride (SF<sub>6</sub>), fluorocarbon (C<sub>2</sub>F<sub>6</sub>), and silicon tetrafluoride (SiF<sub>4</sub>). The gas concentration, 15 the etching time, and the heating temperature can be determined according to the intended degree of etching. The etching gas may be mixed with Cl<sub>2</sub>.

Before the etching step, a preliminary drying step may be provided to dry the inside of the glass pipe. This step can prevent the formation of a highly acidic liquid due to the reaction between the etching gas and H<sub>2</sub>O. In particular, 20 when SF<sub>6</sub> is used for the etching, if H<sub>2</sub>O remains in the pipe, concentrated sulfuric acid is formed. It is difficult to remove the concentrated sulfuric acid. As a result, impurities such as OH groups intrude into the produced optical fiber. Furthermore, the formation of the concentrated sulfuric acid is ex-

tremely hazardous to the workers.

In the present invention, before the drying step, desirably between the etching step and the drying step, a step may be performed to deposit a glass layer on the inner surface of the glass pipe by using a method such as the modified 5 chemical vapor deposition method (MCVD method) or the plasma-activated chemical vapor deposition method (PCVD method) (this step is called a "glass-depositing step"). For example, the following gases are introduced into the glass pipe 1 from its one end: (a) a material gas for the glass composed of silicon tetrachloride ( $\text{SiCl}_4$ ), (b) a material dopant gas for controlling the refractive 10 index composed of a gas such as germanium tetrachloride ( $\text{GeCl}_4$ ), phosphorus oxychloride,  $\text{SiF}_4$ , or boron trichloride, (c) an  $\text{O}_2$  gas, and (d) an He gas. A heat source is provided at the outside of the glass pipe so as to be able to move relatively to the glass pipe. The heating of the glass pipe with the heat source forms a glass layer on the inner surface of the glass pipe. The types of the 15 heat source include an oxyhydrogen burner, a plasma flame, and an electric furnace such as an induction furnace or a resistance furnace.

The inside of the etched glass pipe is almost free of hydrogen atom-containing substances. In addition, hydrogen atom-containing substances are not adsorbed on the inner surface of the glass pipe. Therefore, the etched 20 glass pipe is eminently suitable as the starting glass pipe for the MCVD or PCVD method. The etched glass pipe can eliminate the need for synthesizing the so-called optical cladding layer. The etched glass pipe is advantageous in that even when a core layer is deposited directly onto the inner surface of the

glass pipe, a high-quality optical fiber can be obtained.

As with the foregoing glass-depositing step, before the drying step, desirably between the etching step and the drying step, a step may be performed to insert a glass rod into the glass pipe (this step is called an "assembling step"). More specifically, the above-described steps may be performed in the following order: the etching step, the glass-depositing step, the assembling step, the drying step, the sealing step, and the collapsing step.

When metallic impurities and other undesirable substances cannot be removed by the drying step only, after the drying step, a step may be performed to chemically purify the pipe by heating it while a gas containing chlorine-element-containing substances is blown through the inside of the pipe (this step is called a "chemically purifying step"). Figure 8 is a schematic diagram showing an embodiment of the chemically purifying step of the present invention. A glass pipe 1 is heated with a heat source 3 at about 1,000 °C while introducing the following gas into it from a gas line 5. The gas is a reactive gas such as Cl<sub>2</sub>, SOCl<sub>2</sub>, SiCl<sub>4</sub>, GeCl<sub>4</sub>, or carbon tetrachloride (CCl<sub>4</sub>). This process can transform a metal and a metal oxide having a low vapor pressure into a metal chloride having a high vapor pressure so that they can be removed (for example, nickel chloride has a vapor pressure of 1 atm at 993 °C and iron chloride has a vapor pressure of 1 atm at about 1,020 °C).

After the chemically purifying step, a step may be performed to dry the inside of the glass pipe (this step is called an "additional drying step"). The reason is that Cl<sub>2</sub> used in the chemically purifying step usually contains 1 ppm or so H<sub>2</sub>O

and it is desirable to remove the H<sub>2</sub>O.

After the drying step or after the drying step and the chemically purifying step, a step is provided to seal the glass pipe or the holding pipe at the side for the gas-discharging end (this step is called a "sealing step"). Figures 9A and 5 9C are schematic diagrams showing an embodiment of the sealing step of the present invention. As shown in Fig. 9A, the glass pipe 1 is heated with a heat source 3 placed at the outside of the pipe to seal the glass pipe 1 by fusion at the end portion. Instead of the fusion bonding at the end portion of the glass pipe, as shown in Fig. 9B, a valve 10 in a gas line 6 attached to one end of the glass 10 pipe may be closed to seal the glass pipe so that the gas cannot be discharged. After the sealing step and immediately before the collapsing step, at least one cycle of the cyclic purging may be performed. This operation is highly effective to reduce the amount of the hydrogen atom-containing substances. As explained earlier, the cyclic purging is performed through the following procedure: First, the gas in the glass pipe is discharged to reduce the pressure inside 15 the pipe. Second, a dried gas is introduced into the pipe to raise the pressure inside the pipe.

Figures 10A and 10B are schematic diagrams showing an embodiment of the collapsing step of the present invention. After the sealing step or the foregoing purging cycle, as shown in Fig. 10A, the glass pipe 1 is heated with the moving heat source 3 to collapse it to perform the collapsing step. In this case, a gas, such as Cl<sub>2</sub>, O<sub>2</sub>, a mixed gas of Cl<sub>2</sub> and O<sub>2</sub>, or a mixed gas of Cl<sub>2</sub>, O<sub>2</sub>, and He, may be introduced into the glass pipe 1. It is desirable that the gas con-

tains hydrogen atom-containing substances at a concentration of 10 vol. ppm or less in total. While the gas introduction is maintained, the inside of the glass pipe may be evacuated to reduce the pressure to the range of 100 to 0.1 kPa. This evacuation enables good collapsing without forming gas bubbles at the 5 interface of the collapsing. Alternatively, the inside of the glass pipe may be evacuated without introducing the gas. Yet alternatively, while the gas introduction is maintained, the internal pressure of the glass pipe may be adjusted to become slightly higher than atmospheric pressure. More specifically, it is desirable that the pressure difference between the internal pressure and at- 10 mospheric pressure be +0.01 to +4 kPa, more desirably +0.01 to +1 kPa.

In the embodiment shown in Fig. 10A, the glass pipe 1 and the glass rod 2 are fusion-unified by collapsing. In this case, when the collapsing operation is performed, the inside of the glass pipe 1 is evacuated while a gas, such as Cl<sub>2</sub>, N<sub>2</sub>, or O<sub>2</sub>, is introduced into the pipe. This procedure can reduce the concen- 15 tration of the air intruding into the glass pipe. As shown in Fig. 10B, it is more desirable to provide a gas-introducing port and a gas-discharging port independently at the end of the glass pipe 11.

One of the desirable embodiments of the present invention comprises the following steps in this order: the connecting step, the preliminary drying step, 20 the etching step, the glass-depositing step or the assembling step or both, the drying step, the chemically purifying step, the sealing step, the cyclic-purging operation, and the collapsing step. Thus, a glass rod can be produced.

The glass rod and the glass pipe to be used in the present invention may be

produced with the vapor-phase axial deposition method (VAD method), the modified chemical vapor deposition method (MCVD method), the outside vapor deposition method (OVD method), or another well-known method. It is also desirable that the glass rod produced by performing the collapsing operation of  
5 the present invention be used as the starting glass rod. Alternatively, the glass rod produced by the present invention may be transformed into a pipe through a hollow-forming processing such as boring. The glass pipe thus produced can be used as the starting glass pipe to be collapsed again by re-performing the present invention. This is another form of the desirable em-  
10 bodiments.

When a solid glass body produced with the VAD method is processed into a glass pipe, it is desirable to draw the glass body before it is bored, rather than boring it before it is drawn. If the glass body is first bored to form a glass pipe, when the glass pipe is heated at the time of the drawing, the water adsorbed on  
15 the inner surface of the glass pipe diffuses into the wall of the glass pipe. The diffused water is difficult to remove. When the glass body is drawn before it is bored, it is desirable to etch the inner surface of the glass pipe in a subsequent step such that the inner-surface portion of the glass pipe is rather deeply (for example, one or two mm) removed.

20

#### Example 1

Figure 6 shows a flow chart for Example 1.

1) A silica-glass body was produced with the VAD method. The body was do-

ped with 27 mol % germanium oxide ( $\text{GeO}_2$ ) in the vicinity of the center. The body was processed into a glass rod having a diameter of 7.5 mm and a length of 600 mm. The glass rod was to be used to form the core region.

2) A silica-glass body doped with 1.5 wt. % fluorine was produced with the VAD

5 method. The body was processed into a glass pipe having an outer diameter of 40 mm, an inner diameter of 8.5 mm, and a length of about 500 mm. The glass pipe was to be used to form the depressed region. The concentration of the OH groups in the glass pipe was below the detection limit (0.01 wt. ppm) of the infrared spectroscope. The glass pipe was gas phase-etched by heating it  
10 at about 1,500 °C while an etching gas composed of  $\text{SF}_6$  was blown through the pipe.

3) The glass rod prepared in 1) was inserted into the glass pipe prepared in 2).

4) As shown in Fig. 1B, the glass pipe was evacuated with a vacuum pump through the gas line 6 while a dried  $\text{N}_2$  gas was blown into it at a rate of 2,000

15 "scm" from the gas line 5. The term "scm" is the abbreviation of "standard cubic centimeter per minute." The dried  $\text{N}_2$  gas contained  $\text{H}_2\text{O}$  at a concentration of less than 0.5 vol. ppm and other hydrogen atom-containing substances at a concentration of less than 0.1 vol. ppm. This operation maintained the internal pressure of the glass pipe 1 at 2.5 kPa. During this operation, the  
20 glass pipe 1 and the glass rod 2 were heated with the tape heater 7' at 200 °C.

The heated range included not only the range to be heated at 550 °C or higher in the chemically purifying step, sealing step, and collapsing step to be performed afterward but also an additional length of 200 mm from each end of the

foregoing heating range. The volume of the N<sub>2</sub> gas blown per minute was about 40 times the inner volume of the glass pipe 1 in the heating range (about 50 cm<sup>3</sup>). This operation was maintained for four hours as the drying step. (This step is referred to as the first drying step to distinguish it from the second drying step described in 12) below.)

5 5) As shown in Fig. 8, a Cl<sub>2</sub> gas was introduced into the glass pipe 1 at a flow rate of 500 sccm. Under this condition, the glass pipe 1 was heated with the heat source 3 up to 1,150 °C to remove metallic impurities.

6) As shown in Fig. 9A, a portion in the vicinity of the gas-discharging end of 10 the glass pipe 1 in the drying step was heated with the heat source 3 to seal it by fusion.

7) The inside of the glass pipe 1 was evacuated with a vacuum pump through the gas line 8 to attain a vacuum with a pressure of less than 0.01 kPa. Under this condition, a dried N<sub>2</sub> gas was introduced into the glass pipe 1. Then, the 15 operation of the vacuum pump was stopped to raise the pressure to 105 kPa. This cycle was repeated three times to desorb the adsorbed gas (mainly H<sub>2</sub>O) from the surface of the glass rod 2 and the inner surface of the glass pipe 1.

8) As shown in Fig. 10A, the glass pipe 1 and the glass rod 2 were unified by 20 collapsing the glass pipe 1 to obtain a glass body having a diameter of about 39 mm and a length of 400 mm. During this collapsing operation, a Cl<sub>2</sub> gas was introduced into the glass pipe 1 at a rate of 500 sccm and an O<sub>2</sub> gas, at a rate of 500 sccm. The internal pressure of the glass pipe 1 was -1 kPa against atmospheric pressure. During this collapsing operation, the temperature of the

outer surface of the glass pipe 1 was 1,600 °C when measured with a radiation thermometer.

9) The glass body was drawn to a diameter of 11.7 mm. Then, its circumference was mechanically ground to obtain a glass rod having a diameter of 6.4 mm and a length of 600 mm.

10) A silica-glass body doped with about 0.9 wt. % fluorine was produced with the VAD method. The body was processed into a glass pipe having an outer diameter of 43 mm, an inner diameter of 9 mm, and a length of about 500 mm.

The glass pipe was to be used to form the cladding region. Before the collapsing operation, the glass pipe was gas phase-etched by heating it at about 1,500 °C while an SF<sub>6</sub> gas was blown through the pipe.

11) The glass rod prepared in 9) was inserted into the glass pipe prepared in 10).

12) A dried N<sub>2</sub> gas was blown into the glass pipe at a rate of 2,000 sccm from its one end. Under this condition, the gas inside the glass pipe was discharged from the other end such that the pressure inside the glass pipe could maintain slightly higher than the outside pressure. This operation maintained the internal pressure of the glass pipe at 103 kPa. During this operation, the glass pipe was heated with a tape heater at 170 °C. The heated range included not

20 only the range to be heated at 550 °C or higher in the chemically purifying step, sealing step, and collapsing step to be performed afterward but also an additional length of 200 mm from each end of the foregoing heating range. The volume of the N<sub>2</sub> gas blown per minute was about 35 times the inner volume of

the glass pipe in the heating range (about 60 cm<sup>3</sup>). This blowing-away purging was maintained for one hour as the drying step. (This step is referred to as the second drying step.)

13) A Cl<sub>2</sub> gas was introduced into the glass pipe at a flow rate of 1,000 sccm.

5 Under this condition, the glass pipe was heated up to 1,120 °C to remove metallic impurities.

14) A portion in the vicinity of the gas-discharging end of the glass pipe was sealed.

15) A cyclic purging was performed under the same conditions as in 7).

10 16) As shown in Fig. 10A, the glass pipe and the glass rod treated in 15) were unified by collapsing the glass pipe to obtain a glass body having a diameter of 42 mm and a length of 400 mm. During this collapsing operation, a Cl<sub>2</sub> gas was introduced into the glass pipe 1 at a rate of 100 sccm and an O<sub>2</sub> gas, at a rate of 900 sccm. The internal pressure of the glass pipe 1 was -4 kPa against 15 atmospheric pressure. During this collapsing operation, the temperature of the outer surface of the glass pipe 1 was 1,500 °C.

17) Silica glass doped with about 0.9 wt. % fluorine was synthesized over the circumference of the glass body by using the OVD method. This operation increased the ratio "D/2a" to 43.1, where "D" is the outer diameter of the cladding region and "2a" is the diameter of the core region. Thus, an optical fiber 20 preform was produced. A part of the optical fiber preform was sliced to measure the concentration of the OH groups remaining at the portion formed by the interface portion at the time of the collapsing performed in 8). The measure-

ment was conducted with the infrared absorption method, and the result was 15 ppb.

18) The optical fiber preform was drawn to obtain an optical fiber having a glass-portion diameter of 100  $\mu\text{m}$ . Figure 13 shows the refractive-index profile 5 of the produced optical fiber.

The optical fiber had the following transmission characteristics at a wavelength of 1,550 nm: a transmission loss of 0.50 dB/km, a chromatic dispersion of -41 ps/km/nm, a dispersion slope of -0.01 ps/km/nm<sup>2</sup>, an  $A_{\text{eff}}$  of 8.5  $\mu\text{m}^2$ , a cutoff wavelength of 1,050 nm, and a PMD of 0.1 ps/km<sup>1/2</sup>. These characteristics

10 proved that the optical fiber was highly non-linear. The optical fiber had good properties as an optical fiber for Raman amplification. The transmission loss-wavelength property of the optical fiber is shown by a solid line in Fig. 14. As can be seen from Fig. 14, the excessive transmission loss due to the OH group 15 in the 1.4- $\mu\text{m}$  band (OH-originated loss) is suppressed to less than 0.1 dB/km at a wavelength of 1.38  $\mu\text{m}$ .

#### Comparative example 1

An optical fiber was produced with the same method as in Example 1 except that the first drying step (step 4)) and the chemically purifying step (step 5)) 20 using Cl<sub>2</sub> were omitted. The transmission loss-wavelength property of the optical fiber is shown by a broken line in Fig. 14. As can be seen from Fig. 14, the OH-originated loss was 1.3 dB/km.

**Example 2**

Figure 7 shows a flow chart for Example 2.

- 1) A silica-glass body was produced with the VAD method. The body was doped with 22 mol %  $\text{GeO}_2$  in the vicinity of the center. The body was processed into a glass rod having a diameter of 8.5 mm and a length of 600 mm. The glass rod was to be used to form the core region.
- 2) A glass pipe doped with 1.5 wt. % fluorine was prepared with the same method as in Example 1. The glass pipe had an outer diameter of 40 mm, an inner diameter of 8.5 mm, and a length of about 500 mm. The glass pipe was to be used to form the depressed region.
- 3) A holding pipe was connected to each end of the glass pipe with an oxyhydrogen-flame burner used as the heat source. The connection work was performed on a horizontal glass-processing lathe. The holding pipe had an outer diameter of 40 mm, an inner diameter of 10 mm, and a length of about 400 mm.
- 15 The concentration of the OH groups contained in the holding pipe was 8 wt. ppm when measured with an infrared spectroscope. As shown in Fig. 4A, when the glass pipe and the holding pipe were connected, a dried  $\text{N}_2$  gas was blown into each pipe from the end opposite to the end to be connected.
- 4) The inside of the glass pipe was evacuated with an oil rotary vacuum pump to reduce the absolute pressure to 40 Pa. Subsequently, a dried  $\text{N}_2$  gas was blown through the pipe. During this blowing-away operation, the absolute pressure in the glass pipe was about 102 kPa. The cycle of the pressure reduction and the blowing away was repeated three times to discharge hydrogen

atom-containing substances in the atmosphere in the pipe and hydrogen atom-containing substances adsorbed on the inner surface of the pipe. This was the preliminary drying step.

- 5) A gas-phase etching operation was performed by heating the glass pipe with  
5 a plasma burner while an SF<sub>6</sub> gas was blown into the pipe at a rate of 100 sccm,  
a Cl<sub>2</sub> gas at a rate of 200 sccm, and an He gas at a rate of 100 sccm. During  
this operation, the pipe was moved to reciprocate a plurality of times until the  
inner diameter of the pipe in the effective portion became 11 mm.
- 6) The glass rod prepared in 1) was inserted into the pipe prepared in 5). The  
10 inside of the pipe was evacuated with a vacuum pump to attain a vacuum with  
a pressure of less than 0.1 kPa. Under this condition, a dried N<sub>2</sub> gas was in-  
troduced into the glass pipe. Then, the operation of the vacuum pump was  
stopped to raise the pressure to 103 kPa. This cycle was repeated three times  
to desorb the adsorbed gas from the surface of the glass rod and the inner sur-  
15 face of the glass pipe. During this operation, the glass pipe was heated with a  
mantle heater at 450 °C. The heated range included not only the range to be  
heated at 550 °C or higher in steps to be performed afterward but also an addi-  
tional length of 300 mm from each end of the foregoing heating range. Then, a  
Cl<sub>2</sub> gas was introduced into the pipe at a flow rate of 500 sccm. Under this  
20 condition, the glass pipe was heated up to 1,200 °C to remove metallic impuri-  
ties.

- 7) The clearance between the glass pipe and the glass rod was sealed by using a  
plasma flame as the heat source. Then, the glass pipe and the glass rod were

unified by collapsing the glass pipe to obtain a glass body having a diameter of 39 mm and a length of about 400 mm. During this collapsing operation, the glass pipe was evacuated with a vacuum pump capable of reducing the pressure to 0.03 kPa while a dried O<sub>2</sub> gas was introduced into the pipe at a rate of 5 400 sccm. The dried O<sub>2</sub> gas contained H<sub>2</sub>O at a concentration of less than 0.5 vol. ppm and other hydrogen atom-containing substances at a concentration of less than 0.1 vol. ppm. During this operation, the internal pressure of the pipe was about 0.1 kPa and the temperature of the outer surface of the glass pipe was 1,200 °C. A measurement revealed that the amount of air intrusion into 10 the glass pipe was about 0.01 sccm.

8) The glass body was drawn to a diameter of 13.7 mm. Then, its circumference was processed by mechanical grinding and etching with a hydrogen fluoride solution to obtain a glass rod having a diameter of 9.6 mm and a length of 600 mm.

15 9) A silica-glass body doped with 3 wt. % chlorine (Cl) was produced with the VAD method. The body was drawn to attain a uniform diameter and provided with a hollow at its center. Thus, the body was processed into a glass pipe having an outer diameter of 45 mm and a length of about 650 mm. The glass pipe was to be used to form the cladding region. The concentration of the OH groups in the pipe was below the detection limit.

20

10) A holding pipe was connected to each end of the glass pipe produced in 9) by using the same equipment as used in 3). The holding pipe had an outer diameter of 42 mm, an inner diameter of 15 mm, and a length of 400 mm. The

concentration of the OH groups in the holding pipe was about 8 wt. ppm when measured with an infrared spectroscope. When the glass pipe and the holding pipe were connected, a dried N<sub>2</sub> gas was blown into each pipe from the end opposite to the end to be connected.

- 5    11) The same preliminary drying step as in 4) was performed on the glass pipe produced in 10).
- 12) A gas-phase etching operation was performed by heating the glass pipe with a plasma burner while an SF<sub>6</sub> gas was blown away at a rate of 150 sccm, a Cl<sub>2</sub> gas at a rate of 200 sccm, and an He gas at a rate of 100 sccm. During this 10 operation, the burner was moved to reciprocate a plurality of times until the inner diameter of the pipe in the effective portion became 14.5 mm.
- 13) A silica-glass layer doped with 4 mol % GeO<sub>2</sub> on the average was synthesized on the inner surface of the glass pipe by using the MCVD method, which heated the glass pipe with a plasma flame. The silica-glass layer having a 15 thickness of 1.7 mm was to be used to form the ring portion. After this operation, the inner diameter of the glass pipe became 11.2 mm.
- 14) The glass rod prepared in 8) was inserted into the glass pipe. The glass pipe was heated at about 200 °C with a mantle heater while a dried N<sub>2</sub> gas was blown through the pipe at a rate of 5,000 sccm. The heated range included not 20 only the range to be heated at 550 °C or higher in steps to be performed afterward but also an additional length of 250 mm from each end of the foregoing heating range. The volume of the N<sub>2</sub> gas blown per minute was about 44 times the inner volume of the glass pipe in the heating range (about 113 cm<sup>3</sup>). This

operation was maintained for five hours to desorb the adsorbed gas from the surface of the glass rod and the inner surface of the pipe. Then, a Cl<sub>2</sub> gas was introduced into the pipe at a flow rate of 1,000 sccm. Under this condition, the pipe was heated up to 1,200 °C to remove metallic impurities by causing them 5 to react with the Cl<sub>2</sub>.

15) The glass pipe and the glass rod treated in 14) were sealed and unified by collapsing the glass pipe with a method similar to that in 7). Thus, a glass body having a diameter of 43 mm and a length of 500 mm was obtained.

16) Silica glass doped with 3 wt. % Cl was synthesized over the circumference 10 of the glass body by using the VAD method. This operation increased the ratio "D/2a" to 44.64, where "D" is the outer diameter of the cladding region and "2a" is the diameter of the core region. Thus, an optical fiber preform was produced.

17) The optical fiber preform was drawn to obtain an optical fiber having a 15 glass-portion diameter of 125 μm. Figure 15 shows the refractive-index profile of the produced optical fiber.

The optical fiber had the following transmission characteristics at a wavelength of 1,550 nm: a transmission loss of 0.49 dB/km, a chromatic dispersion of -159.5 ps/km/nm, a dispersion slope of -0.65 ps/km/nm<sup>2</sup>, an A<sub>eff</sub> of 17 μm<sup>2</sup>, a cut-off wavelength of 1,380 nm, and a PMD of about 0.05 ps/km<sup>1/2</sup>. 20

The transmission loss-wavelength property of the optical fiber is shown in Fig. 16. As can be seen from Fig. 16, the excessive transmission loss due to the OH group in the 1.4-μm band is suppressed to less than 0.05 dB/km at a

wavelength of  $1.38 \mu\text{m}$ . The optical fiber is a broad-band dispersion-compensating fiber that can compensate the chromatic dispersion of an optical fiber, having a  $1.3\text{-}\mu\text{m}$ -band zero-dispersion wavelength, from  $1.45$  to  $1.62 \mu\text{m}$ . Because the optical fiber is free from the excessive transmission loss due to  
5 the OH group, it has a low transmission loss in the vicinity of  $1.45 \mu\text{m}$ , proving that it has a good transmission property. Furthermore, the optical fiber is suitable for performing Raman amplification.

As a test for proving the property of the optical fiber, the fiber was placed in an  $\text{H}_2$  atmosphere at a concentration of 100% at a temperature of  $80^\circ\text{C}$  for 24  
10 hours. Then, the transmission loss was measured at  $1.38 \mu\text{m}$ . The measured result showed that the increment in the loss was as small as below the measuring limit of  $0.05 \text{ dB/km}$ .

### Example 3

15 1) A silica-glass body doped with 0.4 wt. % chlorine was produced with the VAD method. The body was processed into a glass rod having a diameter of 4 mm and a length of 600 mm. The glass rod was to be used to form the core region and had a relative refractive-index difference of 0.06% to silica glass.

20 2) A silica-glass body doped with 1.0 wt. % fluorine was produced with the VAD method. The body was processed into a glass pipe having an outer diameter of 25 mm, an inner diameter of 4 mm, and a length of about 500 mm. The glass pipe was to be used to form the cladding region and had a relative refractive-index difference of -0.33% to silica glass. The inner surface of the glass pipe

was gas phase-etched by heating it at about 1,500 °C while an SF<sub>6</sub> gas was blown through the pipe.

3) The glass rod prepared in 1) was inserted into the glass pipe prepared in 2).

4) The glass pipe was evacuated with a vacuum pump from its one end while a

5 dried N<sub>2</sub> gas was blown into it at a rate of 2,000 sccm from the other end. This operation maintained the internal pressure of the glass pipe at 2.5 kPa. During this operation, the glass pipe and the glass rod were heated with a tape heater at 200 °C. The heated range included not only the range to be heated at 550 °C or higher in the chemically purifying step, sealing step, and collapsing 10 step to be performed afterward but also an additional length of 200 mm from each end of the foregoing heating range. This operation was maintained for four hours as the drying step.

5) A Cl<sub>2</sub> gas was introduced into the glass pipe at a flow rate of 500 sccm. Under this condition, the glass pipe was heated with a heat source up to 1,150 °C

15 to remove metallic impurities.

6) A portion in the vicinity of the gas-discharging end of the glass pipe in the drying step was heated with the heat source to seal it by fusion.

7) The inside of the glass pipe was evacuated with a vacuum pump to attain a vacuum with a pressure of less than 0.01 kPa. Under this condition, a dried

20 N<sub>2</sub> gas was introduced into the glass pipe. Then, the operation of the vacuum pump was stopped to raise the pressure to 105 kPa. This cycle was repeated three times to desorb the adsorbed gas (mainly H<sub>2</sub>O) from the surface of the glass rod and the inner surface of the glass pipe.

- 8) The glass pipe and the glass rod were unified by collapsing the glass pipe to obtain a glass body having a diameter of about 24.3 mm and a length of 400 mm. During this collapsing operation, a Cl<sub>2</sub> gas was introduced into the glass pipe at a rate of 500 sccm and an O<sub>2</sub> gas, at a rate of 500 sccm. The internal pressure of the glass pipe was -1 kPa against atmospheric pressure. During this collapsing operation, the temperature of the outer surface of the glass pipe was 1,600 °C when measured with a radiation thermometer.
- 5
- 9) Silica glass doped with about 1.0 wt. % fluorine was synthesized over the circumference of the glass body by using the OVD method. This operation increased the ratio "D/2a" to 15, where "D" is the outer diameter of the cladding region and "2a" is the diameter of the core region. Thus, an optical fiber pre-form was produced.
- 10
- 10) The optical fiber preform was drawn to obtain an optical fiber having a glass-portion diameter of 125 μm.
- 15 In this optical fiber, the increment in the transmission loss due to the OH group was 0.03 dB/km at a wavelength of 1.38 μm.

#### Comparative example 2

An optical fiber was produced with the same method as in Example 3 except that step 4) (the drying step) was omitted. In this optical fiber, the increment in the transmission loss due to the OH group was 2.0 dB/km at a wavelength of 1.38 μm.

20

**Example 4**

1) A glass body was produced through steps similar to 1) to 8) in Example 3.

The glass body had a core region made of silica glass doped with 0.35 wt. %

chlorine and a cladding region made of silica glass doped with 1.1 wt. % fluo-

5 rine. The glass body had a diameter of about 44 mm and a length of 400 mm.

The relative refractive-index difference of the core region to the cladding region

was 0.39%.

2) The glass body was drawn to a diameter of 11.7 mm. Then, its circumfer-

ence was ground by mechanical grinding to obtain a glass rod having a dia-

10 meter of 6.4 mm and a length of 600 mm.

3) A silica-glass body doped with about 1.1 wt. % fluorine was produced with

the VAD method. The body was processed into a glass pipe having an outer

diameter of 43 mm, an inner diameter of 9 mm, and a length of about 500 mm.

The glass pipe was to be used to form the outer cladding region. The pipe was

15 gas phase-etched by heating it at about 1,500 °C while an SF<sub>6</sub> gas was blown

through the pipe.

4) The glass rod prepared in 2) was inserted into the glass pipe prepared in 3).

5) A dried N<sub>2</sub> gas was blown into the glass pipe at a rate of 2,000 sccm from its

one end. Under this condition, the gas inside the glass pipe was discharged

20 from the other end such that the pressure inside the glass pipe could maintain

slightly higher than the outside pressure. This operation maintained the in-

ternal pressure of the glass pipe at 103 kPa. During this operation, the glass

pipe was heated with a tape heater at 170 °C. The heated range included not

- only the range to be heated at 550 °C or higher in the chemically purifying step, sealing step, and collapsing step to be performed afterward but also an additional length of 200 mm from each end of the foregoing heating range. The volume of the N<sub>2</sub> gas blown per minute was about 35 times the inner volume of  
5 the glass pipe in the heating range (about 60 cm<sup>3</sup>). This blowing-away purging was maintained for one hour as the second drying step.
- 6) A Cl<sub>2</sub> gas was introduced into the glass pipe at a flow rate of 1,000 sccm. Under this condition, the glass pipe was heated up to 1,120 °C to remove metallic impurities.
- 10 7) A portion in the vicinity of the gas-discharging end of the glass pipe was sealed.
- 8) A cyclic purging was performed.
- 9) The glass pipe and the glass rod treated in 8) were unified by collapsing the glass pipe to obtain an optical fiber preform having a diameter of 42 mm and a  
15 length of 400 mm. The preform had a ratio, "D/2a," of 15, where "D" is the outer diameter of the cladding region and "2a" is the diameter of the core region. During this collapsing operation, a Cl<sub>2</sub> gas was introduced into the glass pipe at a rate of 100 sccm and an O<sub>2</sub> gas, at a rate of 900 sccm. The internal pressure of the glass pipe was -4 kPa against atmospheric pressure. During this collapsing operation, the temperature of the outer surface of the glass pipe was  
20 1,500 °C.
- 10) The optical fiber preform was drawn to obtain an optical fiber having a glass-portion diameter of 125 μm.

In this optical fiber, the increment in the transmission loss due to the OH group was 0.02 dB/km at a wavelength of 1.38 μm. Unlike the glass body in 8 of Example 3, the glass body in 1) of Example 4 was not directly heated with an oxyhydrogen flame. This is the reason why the optical fiber in Example 4 had 5 an increment in the transmission loss smaller than that of the optical fiber in Example 3.

#### Comparative example 3

An optical fiber was produced with the same method as in Example 4 except 10 that the drying steps were omitted. In this optical fiber, the increment in the transmission loss due to the OH group was 1.5 dB/km at a wavelength of 1.38 μm.

In Examples 1 to 4, a tape heater or a mantle heater was used as the heat 15 source in the drying step. However, other heat sources such as an induction furnace, a resistance furnace, and a laser may also be used. An oxyhydrogen-flame burner or a plasma-flame burner was used in the collapsing step. However, other heat sources such as an induction furnace and a resistance furnace may also be used. Instead of the horizontal glass-processing lathe, a vertical 20 apparatus may also be used. When a vertical apparatus whose heat source has an axially symmetrical temperature distribution is used, it is not necessary to rotate the glass pipe and the glass rod. The glass pipe and the glass rod may be produced by using any of the well-known methods in this technical field,

such as the VAD method, OVD method, MCVD method, and collapsing process. The surface purification and the size adjustment of the glass pipe and the glass rod may be performed by chemical etching (gas phase or liquid phase) in place of mechanical grinding.

5

The present invention is described above in connection with what is presently considered to be the most practical and preferred embodiments. However, the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

10 The entire disclosure of Japanese patent application 2003-008627 filed on January 16, 2003 including the specification, claims, drawing, and summary is incorporated herein by reference in its entirety.